

Magnetic frustration in the context of pseudo-dipolar ionic disorder.

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Abstract. - We consider an alternative to the usual spin glass paradigm for disordered magnetism, consisting of the previously unstudied combination of frustrated magnetic interactions and pseudo-dipolar disorder in spin positions. We argue that this model represents a general limiting case for real systems as well as a realistic model for certain binary fluorides and oxides. Furthermore, it is of great relevance to the highly topical subjects of the Coulomb phase and ‘charge ice’. We derive an analytical solution for the ground state phase diagram of a model system constructed in this paradigm and identify magnetic phases that remain either disordered or partially ordered even at zero temperature. These phases are of a hitherto unobserved type, but may be broadly classified as either ‘spin liquids’ or ‘semi-spin liquids’ in contrast to the usual spin glass or semi-spin glass. Numerical simulations are used to show that the spin liquid phase exhibits no spin glass transition at finite temperature, despite the combination of frustration and disorder. By mapping onto a model of uncoupled loops of Ising spins, we show that the magnetic structure factor of this phase acts, in the limit $T \rightarrow 0$, as a sensitive probe of the positional disorder correlations. We suggest that this result can be generalized to more complex systems, including experimental realizations of canonical spin glass models.

Introduction. – Disordered phases of matter may be categorized in terms of the relative importance of frustrated interparticle interactions and quenched positional disorder (‘frustration plus disorder’). For example, if the frustrated interactions are magnetic and the positional disorder is uncorrelated then one arrives at a recipe for a spin glass, a concept which underpins much thinking about the nature of disordered states [1]. However, it seems reasonable to ask if the combination of frustration with *correlated* positional disorder can lead to distinct behaviour that is not encompassed in the usual spin glass paradigm.

Pseudo-dipolar positional disorder is characterised by a two-particle correlation function in reciprocal space, $g(\mathbf{q})$, that decays like a dipole-dipole interaction. It contrasts strongly with conventional disorder, in which $g(\mathbf{q})$ decays like a screened Coulomb interaction (an exponentially cut-off power law). Spontaneously generated pseudo-dipolar disorder occurs in ice rule ferroelectrics [2] and a magnetic equivalent has been observed in spin ice [3]. How-

ever, to our knowledge, there has been no comprehensive theoretical study of the effect of pseudo-dipolar positional disorder on magnetic properties (although Villain has previously discussed the topic in the context of insulating spin glasses [4]). In particular, the effect of varying the relative strengths of competing exchange interactions within a system possessing pseudo-dipolar positional disorder has remained an unsolved problem. Such a study could be relevant, either ideally, or approximately, to many real systems. For example, a combination of ice-rules positional disorder with magnetic frustration could be realised experimentally in certain inverse spinel ferrites [5] or by the family of fluoride pyrochlores, exemplified by CsNiCrF_6 . In these systems two ionic species (e.g. Ni^{2+} , Cr^{3+}) are distributed over the pyrochlore lattice and Anderson showed that by minimizing the Coulomb interaction the distribution of ions should obey the ice rules (although the perfection of the ice rules in these systems has not been experimentally determined). However it is not clear that spin

glass states are a generic property of this experimental class [6, 7]. Hence it is relevant to ask the questions, what kind of magnetic states should one ideally expect, and what are their experimental signatures? Here we consider the case of ideal ice-rules disorder. Such a study is not only of interest to illuminate an alternative to the traditional spin glass paradigm but is also relevant to the concept of the Coulomb phase [9], a general consequence of pseudo-dipolar correlations. Furthermore, there is currently much interest in ‘charge ice’ [10–12], in which mobile electrons can adopt ice-rule configurations, leading to fractional excitations [10]. Our system provides a counterpoint to the electron system, in that has quenched or static charge disorder, which influences dynamical spin degrees of freedom.

The Model. – The model we study consists of equal numbers of two species of classical Heisenberg spins \mathbf{s}_a and \mathbf{s}_b , randomly distributed across the pyrochlore lattice (a cubic array of corner-linked tetrahedra) and subject to the ‘ice rule’ constraint that there are two spins of each type on every tetrahedron. The spins are coupled by Heisenberg exchange parameters that take one of three possible values, J_a , J_b or J_{ab} depending on whether the neighbouring spins are both of type a , both of type b or one of each type respectively. In the case that all spin lengths and exchange parameters are identical, the model reduces to either a pyrochlore lattice ferromagnet or antiferromagnet. While the former orders conventionally, the latter remains in a cooperative paramagnetic state down to $T = 0$ [13] and gives rise to a distinctive pinch-point magnetic structure factor indicative of pseudo-dipolar spin-spin correlations [3, 14–17].

The case where spin and exchange parameters differ is addressed by expressing the spin Hamiltonian as a sum over contributions from individual tetrahedra,

$$H = -\frac{1}{N_T} \sum_{\alpha=1}^{N_T} \left(\sum_{\langle i,j \rangle_{\alpha}} J_{ij}^{\alpha} \mathbf{s}_i^{\alpha} \cdot \mathbf{s}_j^{\alpha} \right). \quad (1)$$

Here N_T is the number of tetrahedra and $\langle i, j \rangle_{\alpha}$ indicates all pairs of spins i and j on plaquette (tetrahedron) α with exchange interaction J_{ij}^{α} .

A single tetrahedron. We begin by focusing on a single tetrahedron and, with no loss of generality, we assign spins \mathbf{s}_1 and \mathbf{s}_2 to be of type a and spins \mathbf{s}_3 and \mathbf{s}_4 to be of type b . We then define three angular variables: ϕ_a as the angle between spins \mathbf{s}_1 and \mathbf{s}_2 ; ϕ_b as the angle between spins \mathbf{s}_3 and \mathbf{s}_4 ; θ as the angle between the resultants $\mathbf{S}_a = (\mathbf{s}_1 + \mathbf{s}_2)$ and $\mathbf{S}_b = (\mathbf{s}_3 + \mathbf{s}_4)$. In these coordinates the Hamiltonian for the single tetrahedron becomes

$$H = -J_a s_a^2 \cos \phi_a - J_b s_b^2 \cos \phi_b - 2J_{ab} s_a s_b (1 + \cos \phi_a)^{\frac{1}{2}} (1 + \cos \phi_b)^{\frac{1}{2}} \cos \theta. \quad (2)$$

The ground state magnetic configurations then separate into two classes, characterized by the sign of J_{ab} , allowing an effective phase diagram to be mapped out in the space

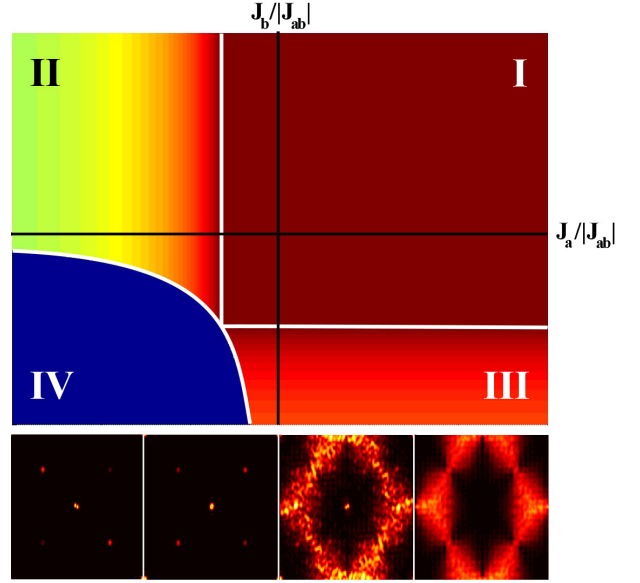


Fig. 1: The four regions of distinct magnetic behaviour (boundaries in white) as a function of the reduced exchange parameters $J_a/|J_{ab}|$ and $J_b/|J_{ab}|$. The boundary defining region IV is universal, $|J_a||J_b| = |J_{ab}|^2$, while the remaining boundaries are defined by the ratios of the spin lengths: $J_a/|J_{ab}| = -s_b/s_a$ between regions I and II; $J_b/|J_{ab}| = -s_a/s_b$ between regions I and III. The background colour is an indication of the value of the ground state sublattice order parameter as defined by equation 5. The bottom panels are the magnetic neutron scattering structure factors, $S(Q)$, in the different regions as discussed in the text ((I-IV displayed left to right, respectively), shown in the $[h, h, l]$ reciprocal space plane from -2 to $+2$ on each axis). For region II, scattering from all spins has been included whereas in region III only scattering from components of the b spins perpendicular to the common a axis is shown (the intensity in this third panel is enhanced slightly relative to other regions in order to reveal the structure of the diffuse scattering). The plots of $S(Q)$ have been obtained from Monte Carlo simulations at the points $(J_a, J_b, J_{ab}) = (1, 1, 1)$, $(-2, 2, 1)$, $(2, -2, 1)$ and $(-2, -2, 1)$ for regions I, II, III and IV respectively (all at $T/|J_{ab}| = 0.1$).

spanned by the reduced variables $J_a/|J_{ab}|$ and $J_b/|J_{ab}|$ (Fig. 1). The topology of the resulting phase diagram is independent of the sign of J_{ab} , as are the equations of the boundaries between regions.

In region I, spins of the same species are aligned parallel. Spins of different species are either parallel or anti-parallel depending on the sign of J_{ab} . This behaviour extends even into the quadrants of J -space where one or both intra-species interactions are antiferromagnetic. The extent of this domination by J_{ab} is governed by the ratio s_a/s_b as indicated by the equations of the boundaries between region I and regions II and III (Figure 1).

Regions II and III are identical on interchanging the labels a and b . In the ground state, spins of one species are perfectly parallel whilst the antiferromagnetic coupling of the other species is frustrated by the coupling J_{ab} . These

spins cant away from the collinear axis defined by the first species through an angle equal to half that between spins of type x ,

$$\cos \phi_x = \frac{2J_{ab}^2 s_y^2}{|J_x|^2 s_x^2} - 1, \quad (3)$$

where $\{x, y\} = \{a, b\}$ ($\{b, a\}$) in region II (III) and $|J_x| > s_y/s_x$. The single species sublattice order parameter is defined in these regions as

$$m^{(x)} = \frac{1}{N_x s_x} \sqrt{\left(\sum_{i \in \{x\}} \mathbf{s}_i \right) \cdot \left(\sum_{i \in \{x\}} \mathbf{s}_i \right)} \quad (4)$$

where N_x is the number of spins of type x and the sum is over all spins of type x (our definition anticipates extending the theory to a macroscopic lattice). Combined with (3) we see that the ground state order parameter is inversely proportional to J_x :

$$m_{\text{gs}}^{(x)} = \frac{s_y |J_{ab}|}{s_x |J_x|}. \quad (5)$$

This order parameter is defined only in terms of the x spins as the y spins are perfectly ordered with respect to each other (parallel or anti-parallel depending on the sign of J_{ab}) throughout regions II and III. Within regions I and IV we simply define $m_{\text{gs}}^{(x)} = 1, 0$ respectively.

In region IV the intra-species antiferromagnetic interactions dominate, leading to configurations with $\phi_a = \phi_b = \pi$. Thus the third term of (2) is zero and the Hamiltonian is independent of θ . In this region, spins of different species are effectively decoupled. For $J_{ab} > 0$ the confluence of the phase boundaries is particularly interesting as at this point the ordered ferromagnet becomes degenerate with the antiferromagnetic spin liquid.

Extension to the macroscopic lattice. Consider now a macroscopic pyrochlore lattice having two A and two B ions per tetrahedron. A walker, starting at some ion of type A and following a path only through sites populated by A ions (without retracing its steps) will always return to its starting point. Furthermore, the path traced out will have no branches but will form a continuous closed loop containing an even number of lattice sites. The whole lattice is tiled with such loops – every lattice site belongs to one (and only one) of these closed, even membered, loops of spins of a single species (referred to simply as ‘loops’ from now on). The statistics of such loops have recently been discussed in the context of the magnetic Coulomb phase [18]. In regions I, II and III, A type loops and B type loops interact with each other via J_{ab} which has the effect of imposing long range order. By contrast, in region IV there is no coupling between loops, although spins within a given loop are perfectly antiferromagnetically ordered with respect to each other. We consider this soup of uncoupled, closed, antiferromagnetic loops to be a novel spin-liquid like phase; frozen interactions within loops exist within a framework of two mobile degrees of freedom

per loop. There are no energy barriers to facilitate global spin freezing and so, in the absence of free energy barriers or dynamical constraints, there can be no spin glass transition in region IV. This is in contrast to the Heisenberg pyrochlore antiferromagnet (HPAFM) with weak random and uncorrelated bond disorder [19,20] to which a number of points in region IV are closely related.

In all regions of J -space, the ground states of the single tetrahedron are robust to stacking, with no extra frustration incurred. The phase diagram in Fig. 1 should therefore be equally valid for the macroscopic lattice.

The decoupling of loops in region IV requires either $\phi_a^\alpha = \pi$ or $\phi_b^\alpha = \pi$ on every tetrahedron α , both of which are true in the ground state. The individual loops may then be viewed as independent one-dimensional Heisenberg chains, which may be arbitrarily long in the thermodynamic limit. For $T > 0$, ϕ_a^α and ϕ_b^α may differ from their ground state values due to the excitation of low energy spin waves. The Hamiltonian then regains its dependence on the variable θ which is likely to dramatically slow the dynamics. Our numerical simulations suggest, however, that this slowing does not amount to truly broken ergodicity. Relaxing the ice rules constraint on the ion placement prevents this dynamical slowing down by providing extra unconstrained magnetic degrees of freedom in plaquettes with all ions of the same species or ions in a 1:3 ratio. It is readily shown that 1:3 and 3:1 tetrahedra place fewer constraints on the magnetic degrees of freedom than do the 2:2 tetrahedra. This result may be understood intuitively given that tetrahedra with all spins of the same species are the least magnetically constrained of all.

Numerical Simulations. – Numerical evidence from Monte Carlo simulations is in agreement with our theoretical predictions. Simulations were performed on lattices with L^3 cubic unit cells ($L = 4, 7$, corresponding to 1024 spins and 5488 spins respectively) for which a short loop algorithm [21] was used to generate ion configurations obeying the ice rules constraint. In all simulations we observed loops on all scales, from the smallest possible (six membered rings) up to loops spanning the system. With one exception (discussed below) the energy scale was defined by $|J_{ab}|$ and a single spin flip Metropolis algorithm was employed, with spin updates confined to a small solid angle.

To investigate spin freezing, we recorded the Edwards-Anderson order parameter

$$q_{\text{EA}} = \frac{1}{N} \sum_{i=1}^N \langle \mathbf{s}_i \rangle^2, \quad (6)$$

in the region $0.01 \leq T/|J_{ab}| \leq 0.1$ with $L = 7$. We chose $s_a = 3/2$, $s_b = 1$, (corresponding to the magnitudes of the magnetic ions in CsNiCrF_6) and focused on the point $(J_a/|J_{ab}|, J_b/|J_{ab}|) = (-1.1, -1.1)$, ensuring three different bond contributions to the energy. We simulated both the completely random and ice rules constrained models

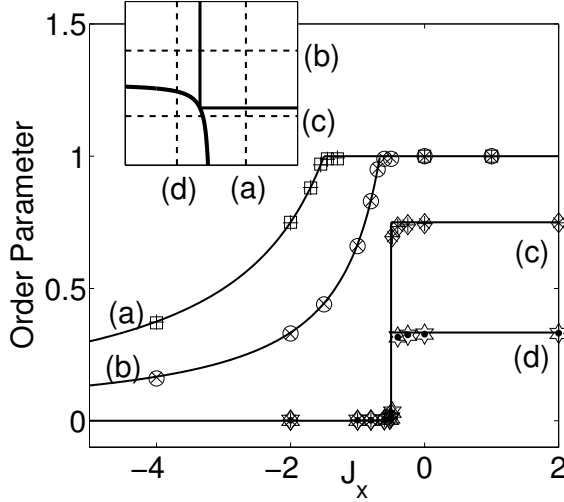


Fig. 2: Variations in the order parameter, $m^{(x)}$, along lines in J -space denoted $(J_a/|J_{ab}|, J_b/|J_{ab}|)$: (a) along $(2, J_b/|J_{ab}|)$; (b) along $(J_a/|J_{ab}|, 2)$; (c) along $(J_a/|J_{ab}|, -2)$; (d) along $(-2, J_b/|J_{ab}|)$. The solid lines represent the theoretical ground state magnetization as given by equation 5 in regions II and III (and defined as 1 in region I and 0 in region IV). The symbols represent the results of Monte Carlo simulations conducted at $T/|J_{ab}| = 0.01$. Line symbols +, x, * and closed circles correspond to $J_{ab} > 0$. Open symbols refer to $J_{ab} < 0$.

as described above. At each temperature the systems were annealed in five steps from $T/|J_{ab}| = 1$ with 10^6 MCS/s (Monte Carlo Steps per spin) (10^7 MCS/s were used at and below $T/|J_{ab}| = 0.03$) for equilibration at each step. Data was recorded over 10^6 (10^7) MCS/s and averaged over ten disorder configurations. In the absence of the ice rules constraint q_{EA} is essentially zero at all the temperatures studied. Imposing the constraint leads to a significant slowing of the dynamics, but with 10^7 MCS/s q_{EA} remains below 0.05 even at $T/|J_{ab}| = 0.01$. As already noted, this behaviour is in strong contrast with that of HPAFM with weak random bond disorder [19, 20].

Figure 2 shows the variation of the order parameter $m^{(x)}$ along the indicated lines in J -space. The agreement between the theoretical and numerical results is striking and this level of accuracy has been achieved with relatively small scale simulations ($L = 4$, $s_a = 3/2$, $s_b = 1$ and MCS/s= 10^6). These results validate the extension of our analytical solution to the macroscopic lattice.

For the macroscopic lattice, differences in the ground state behaviour between the regions should manifest themselves in the magnetic structure factor, examples of which are shown in the lower panels of Figure 1. For region I, long range collinear order produces sharp Bragg peaks. In regions II and III, sharp peaks arise from the components of all spins along the pseudo-collinear axis (shown for region II of Figure 1), however scattering from just the perpendicular component of the canted spins (shown for region III of Figure 1) reveals interesting diffuse scatter-

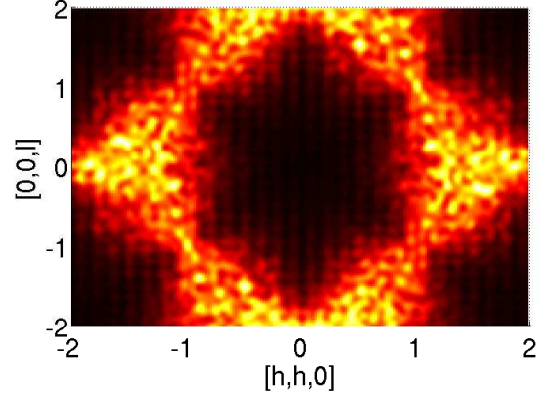


Fig. 3: The magnetic structure factor $S(Q)$ for a system tiled with independent chains of antiferromagnetically coupled Ising spins, each chain with a randomly selected easy axis. This data was obtained using $L = 7$ with averaging over 10 easy axis configurations for each of 50 disorder configurations.

ing that suggests spin liquid like correlations transverse to the ordered component. We suggest that this might be called a ‘semi-spin liquid’, in analogy with a semi-spin glass [4]. In region IV $S(Q)$ has the characteristic structure factor of an algebraic spin liquid, with pinch points indicative of the pseudo-dipolar correlations, although without the same clarity observed previously in studies of the HPAFM [15–17]. The origins of such correlations in our model are not trivial. Unlike the pure HPAFM, the ground state in region IV has spins which interact only within a single loop. For such a ground state to exhibit pinch-point scattering would indicate that dipolar correlations emerge purely as a consequence of the geometric distribution of loops, as governed by the ion configuration. The spin-spin correlation function is then nothing more than the probability that the two spins are on the same loop. To confirm this assertion we examined a toy model representative of the ideal ground state of the system: J_{ab} was set to zero and perfect Néel order was enforced within each loop. We assigned a randomly selected easy axis to each loop and measured $S(Q)$ for the resulting configuration. This process was repeated for a number of sets of randomly chosen easy axes and the resulting structure factors averaged. The resolution was improved by averaging again over a number of disorder configurations. The results (Figure 3) clearly show signs of dipolar spin-spin correlations emerging from this system of magnetically independent $1d$ chains. To obtain the data in this figure we averaged over 50 disorder configurations with $L = 7$. $S(Q)$ was averaged over 10 easy-axis configurations per lattice.

A direct consequence of the above observations is that the magnetic scattering is acting as a probe of the structural disorder. There is however an inherent limit on the resolution of the pinch-point scattering pattern which can result from a single realisation of the quenched disorder

on a finite lattice. Unlike the pure HPAFM, for which the bow-tie pattern is well resolved even for relatively small lattices, the ice rules constrained binary pyrochlore described here has the lengths and spatial arrangement of its loops predetermined by a particular ion configuration. The pure HPAFM however allows for a dynamic interchange of spins between loops, in effect sampling a large number of loop configurations with a corresponding increase in resolution. In practical terms, this should have a similar effect to averaging the quenched disorder over many equivalent ion configurations.

Conclusions. — In conclusion, for the ideal model considered we have demonstrated the suppression of spin glass behaviour and the emergence of novel spin liquid and semi-spin liquid phases. It will be of interest to re-examine the magnetic behaviour of the fluoride pyrochlores in the light of this result. In particular, certain fluoride pyrochlores have been reported to show spin glass transitions [6] however there is a growing body of evidence that these compounds do not form traditional spin glasses below the supposed freezing temperature [7,8,23]. We conclude that if these are true spin glass transitions, they must be a consequence of disorder or interactions beyond those considered here. At a more general level we have illustrated a counter example to the idea that geometric frustration and positional disorder must combine to generate a spin glass, although we have not ruled out the possibility that the spin liquid states we have identified may be highly sensitive to further quenched disorder of a different character. Finally, our results have shed light on an issue of rather general importance that is pertinent to the interpretation of neutron scattering patterns of disordered magnets. Thus, quenched atomic or ionic disorder is generally characterised by an energy scale much higher than that of the magnetic interactions, so the magnetic structure factor should generally be affected by the structural disorder correlations, but the question is to what degree, and what does this signify? We have identified a limiting case where the magnetic and structural disorder correlations are closely connected, and this connection is easily comprehended in terms of the model of ‘unfrustrated’ spin loops we describe. The opposite limiting case, which one would expect to apply to an ideal spin glass, is where the frustration is purely magnetic in origin and there is no dependence of magnetic on structural correlations. Real systems are likely to lie between these two limiting cases, so our results may be of some general relevance to the interpretation of neutron scattering patterns, including those of canonical spin glasses [24] and weakly disordered spin glass systems such as ‘SCGO’ [25] and $\text{Y}_2\text{Mo}_2\text{O}_7$ [26,27].

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